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Maria Dolores FIDELIBUS[1*], Gabriella BALACCO[2], Andrea GIOIA[3], Vito IACOBELLIS[4], Giuseppe SPILOTRO[5]

[1] Dipartimento di Ingegneria Civile, Ambientale, del Territorio, Edile e di Chimica (DICATECh), Politecnico di Bari, Via Orabona 4, 70125 Bari, Italy, Corresponding author: mariadolores.fidelibus@poliba.it, tel: +39 080 5963373

[2] DICATECh, Politecnico di Bari, Via Orabona 4, 70125 Bari, Italy, gabriella.balacco@poliba.it

[3] DICATECh, Politecnico di Bari, Via Orabona 4, 70125 Bari, Italy, andrea.gioia@poliba.it

[4] DICATECh, Politecnico di Bari, Via Orabona 4, 70125 Bari, Italy, vito.iacobellis@poliba.it

[5] Dipartimento delle Culture Europee e del Mediterraneo (DICEM), Università degli Studi della Basilicata, Via Rocco Lazazzera 35, 75100 Matera, Italy, giuseppe.spilotro@unibas.it

ABSTRACT

This study aims at recognizing the mechanisms of mass transport between the karst surface and the saturated zone in a morpho-structural relief of the Mesozoic karst carbonate platform of Murgia (Puglia, Southern Italy). The large dimension of the karst aquifer, the regional scale of the flow system, the boundary condition constituted by the sea, and the lack of freshwater springs constrain to the use of wells as monitoring points and limit the study area to the recharge area comprising 986 endorheic basins.

The concentrations of non-reactive tracers (nitrates) in the waters of autogenic recharge (from endorheic basins) have been modelled through the evaluation of effective infiltration, land use, and nitrogen surplus, with reference to a time window, which includes a low precipitation period followed by significant rainfall events. The comparison between the modelled nitrate concentrations and the nitrate concentrations measured in ground waters, coupled with the analysis of groundwater chemograms and records of hydraulic heads (all referred to the same time window), allows inferring the mechanism of mass transport between the karst surface and the groundwater table. The mass transport conceptual model requires the presence of the epikarst. The infiltration of significant rainfall in the endorheic basins after a low precipitation period displaces waters stored in the epikarst towards the saturated zone. Ground waters in the post-evet period show higher concentrations of nitrates, lower concentrations of Total Organic Carbon and higher Mg/Ca ratios than both those of the pre-event period and the autumn-winter recharge period. The post-event recharge from epikarst storage determines a transient hazard of groundwater pollution with a time lag from the occurrence of the heavy rainfall.

Key words: *platform karst, epikarst, endorheic basin, heavy rainfall, mass transport, nitrates,*

Running head:
Epikarst under heavy rainfall causes temporary groundwater pollution

1. INTRODUCTION

The volume of effective infiltration, the structural, physical and chemical characteristics of unsaturated zone, as well as the extent and space-time distribution of pollutant loads on ground surface are the main factors that control the mass transport from karst surface to saturated zone. Amount and trend of precipitation, atmospheric temperature, surface morphology and soil features are implicitly included in the calculation of effective infiltration. Due to the intrinsic complexity of each karst aquifer structure, the mechanisms of recharge and mass transport may differ among different karst aquifers and within a same karst aquifer. However, the interpretation of the hydraulic behaviour and the chemical features of ground waters under a hydrological stress, such as that caused by significant rainfalls following drought or low recharge periods, allows inferring mass transport mechanisms.

This study aims at identifying the mechanism of mass transport between the karst surface and the saturated zone in a coastal karst aquifer through a semi-quantitative approach. The major focus is on the role played by the epikarst, which is one of the four sub-systems besides soil, unsaturated zone and saturated zone, which compose a karst system. Each sub-system has its own specialness in terms of flow and transport processes.

Mangin (1974a, 1974b, 1975) first defined the "epikarstic aquifer" as a leaky perched saturated zone, located within the superficial part of the karst, able to store infiltrating water. The term "epikarst" that generalize the above concept, represents a permeable (due to fractures and cracks) karst zone overlying the carbonate bedrock, which show normally fine fissures and vertical joints. The thickness and the hydraulic properties of the epikarst depend on the geological history, climate and plant cover (Mangin, 1975, Blavoux and Mudry, 1983; Williams, 1983; Drogue, 1992; Bakalowicz, 1995; Jeannin, 1998; Dörfliger et al., 1999).

Because of its usual high storage capability, the epikarst can hold up percolation water and pollutants during their migration towards the saturated zone during dry or low recharge periods. Chemical features of water stored in the epikarst normally differ from those of the original percolation water, depending on residence time (of weeks or months) and attenuation processes on stored organic loads (Batiot *et al*., 2003; Mudarra and Andreo, 2010). In particular, both magnesium (parameter indicating the extent of dissolution in carbonate aquifers) and nitrate (non-reactive pollutant) concentrations increase in the stored waters compared to concentrations in the original water, while concentrations of Total Organic Carbon (TOC) decrease.

During recharge periods following dry or low recharge periods, the incoming water mixes with residing water while leaching stored pollutants. When the epikarst saturates (infiltration rate exceeding percolation rate) water quickly moves towards the saturated zone through the main discontinuities and/or conduits (Gunn, 1983; Klimchouk, 2004). After flushing, the additional percolation water will flow through the unsaturated (transition) zone, characterized by fractures, joints and inter-granular seepage.

With regard to the karst aquifer of Murgia (Puglia, southern Italy, Figure 1), this study addresses three main research questions: a) does the epikarst control infiltration, recharge and mass (pollutant) transport, b) can we use the information on mass transport mechanisms for outlining groundwater pollution hazard, and c) which methodological approach should be used to recognize such a control?

The study is special because the Murgia aquifer belongs to a platform karst characterized by thick and large sedimentary complex, formed by horizontal and gently sloping strata and platform relief (as in Milanovic, 2004 and Stevanovic, 2015). Moreover, the sea partly borders the huge karst aquifer that behaves as a coastal aquifer: consequently a transition zone and salt waters are found at the bottom of fresh groundwater depending on the value of the hydraulic heads. The aquifer shows a high anisotropy of the intrinsic permeability, due to the complex network of discontinuities, and surface and subsurface karst forms. Not last in importance, the groundwater flow system is of regional type (according to the definition of Toth, 1963). Groundwater discharge occurs only along the coast as diffuse flow or through coastal and submarine brackish springs: there are no freshwater springs.

The size of the aquifer and the regional flow system involve a delayed response time of groundwater to any hydrological stress: in karst aquifers of smaller size, this response occurs instead in a short time from the hydrological stress.

Considering all the geological and hydrogeological features, it is clear that the scenario does not allow answering above research questions with the application of the usual methodologies used in the karst research, but it requires a technical and innovative methodological approach.

Thus, to answer above questions, the study considers the following features of the study area with an inter-disciplinary view: (i) the geomorphological characteristics; (ii) the thermal field of the aquifer; (iii) the hydrological factors; (iv) the land use; (v) the chemical characteristics of ground waters (sampled in wells) and (vi) the hydraulic heads of groundwater. The (i) and (ii) features allow selecting the hydrogeological basins located in the main recharge areas, while the (iii) and (iv) features lead to model effective infiltration and nitrate concentrations in recharge water within the hydrogeological basins, with reference to a time interval characterized by a low recharge period and a consecutive wet period. The (v) and (vi) features, regarding the same time window, were used to validate the results of modelling.

2. STUDY AREA

2.1 Geological and morphological features

The study area (Alta Murgia, also known as Murge Alte, Figure 1) corresponds to the NW part of Murgia region and includes a National Park (of about 68,000 ha) instituted in 2004. Alta Murgia is a plateau developed along the NW-SE direction (15 ÷ 25 Km large and 70 ÷ 90 Km long), which is bordered by old coastlines. Its elevation ranges from 450 up to max 680 m a.s.l.. The plateau is part of a wider area named Murgia, a morpho-structural high that is, in turn, part of the Apulian carbonate platform, the upper part of the Apulian Foreland, emerged during Cretaceous (Pieri *et al.,* 1997). Murgia represents the outcrop of a Cretaceous carbonate succession (Figure 1) about 3 km thick that shows SW and SSW dip directions (Ricchetti, 1980; Ciaranfi *et al*., 1988; Ricchetti *et al*., 1988). The main formations of this succession are known as "Bari

Limestone" (Valanginian–Early Turonian?), outcropping to the N and about 2000 m thick, and "Altamura Limestone" (Senonian), about 1000 m thick, which outcrops to the S (Ricchetti, 1980, Ciaranfi *et al*., 1988). Discontinuous thin calcarenite, sand, and clay transgressive deposits of late Pliocene–Quaternary cover the Cretaceous formation.

<Figure 1>

Tectonic stress fields caused deformation and rupture patterns from Cretaceous to Pleistocene. The N and the SE sectors of Murgia are respectively characterized by large regional normal faults with a NW-SE trend, progressively arching to WNW-ESE and by oblique transfer faults with E-W trend (Pieri *et al.*, 1997; Billi and Salvini, 2003; Festa, 2003; Spalluto *et al.*, 2007). The major normal fault system is accompanied by perpendicular minor faults and gentle synclines and anticlines. Besides the normal NW-SE oriented faults, Korneva *et al.* (2014) have also recently inferred NNW-SSE striking left-lateral and WNW-ESE striking right-lateral strike-slip faults, which should represent Upper Cretaceous synsedimentary faults, while WNW-ESE striking, left-lateral faults and NE-SW striking normal faults should be interpreted as Pliocene-Quaternary faults associated to the flexure of the Apulian foreland (Doglioni *et al.*, 1994).

In the geological time, the coupling of tectonic subsidence (and/or uplift) and eustatism controlled both water table elevation and vertical and horizontal fluctuations of the transition zone, as well as the thickness of the vadose zone: such fluctuations engendered the genesis and evolution of both subsurface and surface karst morphologies (Canora *et al.*, 2012). The regional subsidence-driven transgression, which occurred during the Plio-Pleistocene, transformed the Apulian Foreland in an archipelago (Tropeano and Sabato, 2000; Mateu-Vicens *et al.*, 2008). At the maximum of transgression, only two large areas emerged: they are presently bounded by the old coastline at 425 - 450 m a.s.l. (Pieri *et al*., 1997; Canora *et al*., 2012) and correspond to Alta Murgia. According to the palaeo-geographic history, an aquifer thickness of roughly 200-250 m should have been subject only to vadose diagenesis in correspondence of this area, while some 400 m in the central part of Alta Murgia should have remained unaffected by seawater and brackish water, hypothesizing a max hydraulic head of 10 m above the related sea level (at the maximum regional subsidence-driven transgression.

Alta Murgia plateau actually shows a quite flat morphology, with a number of natural endorheic basins, which are internal drainage basins; moreover, it shows a high density of deep sinkholes within a mainly bare karst. Sauro (1991, 2012) describes the Alta Murgia plateau as a honeycomb system of large karst depressions, classified as low relief cockpits, relicts of the morphogenetic phase developed on the exposed platform during the late Tertiary and Quaternary (Neboit, 1975; Grassi *et al*., 1982; Sauro, 1991). The endorheic basins of Alta Murgia play a significant role in the hydraulic regime of the area because of their peculiar hydrologic behaviour. Usually, they are considered as a series of small sub-basins independent from each other: nevertheless, in case of extreme events their surface-water storage capability can be exceeded, originating cascade flows towards other downstream sub-basins (Iacobellis *et al.*, 2015).

Shallow valleys (*lame*) generally filled with thin alluvial and residual deposits (*terra rossa*) characterize the surface hydrographic pattern of the Alta Murgia plateau. *Terra rossa* irregularly fills up fissures, pockets and karst hollows: this way, the different surface textures can either delay the triggering of runoff and infiltration or fully inhibit runoff in the bare karst (Canora *et al.*, 2008). The complex hydrological behaviour of natural surface and epikarst textures has been made far more complex by stone shattering extensively used in the last decades (i.e. the flattening and modification of karst original textures made in relation to the change of land use from pasture to sown land, Canora *et al.*, 2008). Agricultural practices of removing and crushing the karst surface with contemporary addition of fine graded soils have produced significant alterations in valley morphologies, drainage networks, vegetation and soil characteristics, with consequent changes of effective infiltration and natural flood control in the whole area. The damages deriving from such extensive land use changes have become dramatically evident in a short time, with increase of surface runoff, flood frequency and peak flow volumes: however, fine soils have been later eroded, rapidly turning the stone shattered fields into degraded lands without cultivations, with recovering of effective infiltration.

The study area has a Mediterranean climate, with strong inter-annual variability and a marked annual seasonality; the thermometric regime (1950-2002) is characterised by maximum monthly values of 24.8°C between June and August and minimum monthly values of 7 °C between December and February. The mean yearly precipitation is 651,8 mm/y (1950-2002, Portoghese *et al.*, 2010): precipitation is distributed quite irregularly over the year, with peaks in the October-March semester. During last few decades, climate variations consist in the increase in length and frequency of dry periods with alternation of short precipitation events of high intensity.

2.2 Hydrogeology

The Cretaceous carbonate platform of Murgia is bordered to the S and to the NE by the Ionian and Adriatic Sea respectively; to the W and SW the cover sediments act as geological no-flow border, which forces groundwater flow to the S. The Cretaceous karst formation comprises a coastal groundwater, which flows towards the coasts and to the SE towards a contiguous hydrogeological unit. Discharge into the sea occurs through diffuse flow or focused brackish springs, according to permeability features along the coasts: this is due to the geomorphological features of the platform karst aquifer, the regional scale of its flow system, and the boundary conditions due to seawater.

The complex network of main and minor fractures, stratification joints and conduits, the uneven presence of residual soils along discontinuities, and the variable permeability of the different carbonate Cretaceous formations entail a high anisotropy of the hydraulic conductivity (Fidelibus *et al.* 2010): groundwater, often locally confined, mainly flows according to preferential flow-pathways. Main recharge areas are located at the highest elevations of the region, where the numerous endorheic basins provide a focused autogenic recharge. Somewhere inland, the piezometric heads reach 200 m a.s.l.. The piezometric gradient varies in the range 1.5‰–8‰.

The chemical composition of fresh ground waters of the Murgia aquifer derives mainly from water-carbonate rock interaction. The Total Dissolved Solids (TDS) content varies from 0.2 to 0.6 g/L. Ground waters with TDS>0.6 g/L are found in the coastal part of the aquifer and close to the NW and SE borders of the region, where the carbonate basement is sunk due to normal faults under the Plio-Pleistocene covers. Groundwater exploitation started in the 1960s, with a consequent progress of groundwater salinization (both due to present seawater and old saline waters of marine origin), mainly in the fragile coastal zone. Inland, the high hydraulic heads prevent the presence of saltwater under fresh groundwater.

3. METHODOLOGICAL STEPS AND CONSTRAINTS

The study develops according to a few main steps, driven by a few constraints.

The study develops according to some main steps, driven by a few constraints determined in turn from the methodological approach. This approach requires that: (i) the study is carried out within a recharge area with a network of monitoring wells (given the unavailability of karst springs as measuring points) for the study of the quality of waters along a substantially vertical path between karst surface and the surface of the saturated zone; (ii) that it is possible to select a time window for which occurs at the same time a condition of hydrological stress and the existence of the monitoring data with appropriate frequency. Such limiting conditions, together with the other constraints below detailed, lead to select the recharge area of Alta Murgia and a time window related to the years between 1994 and 1995.

The first constraint to consider is the presence of endorheic basins in the study area. The calculation of the effective infiltration and runoff in Alta Murgia entails a model able to consider not only the absorption capacity of different karst surface textures, but also the hydrologic behaviour of endorheic areas. The calculation of effective infiltration calls for a clear delimitation of the hydrogeological basins, which are mostly of endorheic type (first constraint of the study). Such basins have not been so far delimited: the River Basin Authority only locates flow accumulation points in the Hydro-geo-morphological Map of Puglia Region (Autorità di Bacino della Puglia, 2009).

The second constraint regards the points where to monitor groundwater. This research has to focus on wells, due to the lack of freshwater springs, and on inland areas of the aquifer where groundwater is not affected by saltwater intrusion. Actually, the outlet of a freshwater spring is the classical site where karst hydrogeologists study the so-called "global response" of the karst aquifer to obtain information about the presence and role of the different karst sub-systems in recharge processes (Kiraly, 2003). Water derived from direct infiltration of precipitation is seldom observed at springs, because recharge mostly occurs through the mediation of the sub-systems of the unsaturated zone (Aquilina *et al.*, 2005, 2006); in most cases, the chemical imprints of epikarst water are clearly distinguishable from those featuring water from other reservoirs. The classical study approach involves a high frequency monitoring of hydraulic, physical, chemical and isotope features of water discharging from karst springs during both high and low flows. Differently from typical situations, Murgia groundwater discharges only through diffuse coastal flow or focused brackish coastal springs. Thus, studies on fresh ground waters in

Murgia region cannot rely on freshwater springs, but only on very deep wells (with length higher than 500 m) located inland far from the influence of sea- or salt-waters. While freshwater springs allow monitoring and sampling at a unique point with high time frequency, such wells, only allow sampling at discrete depths and borehole-logging with low time frequency.

The third constraint of the study entails the control of the correspondence between the endorheic basins and sub-basins and the recharge areas, where infiltration water follows a substantial vertical path from the surface to the saturated zone. This feature implies the direct relation between the chemical features of the autogenic recharge water from the endorheic basins and those at water table. Hence, the distribution of endorheic basins in the study area is compared to the distribution of recharge areas inferred from the interpretation of the thermal field of the aquifer (Fidelibus *et al.*, 2010).

The availability of groundwater monitoring wells, located inside or close to endorheic basins, having the maximum chance to intercept directly the autogenic recharge flow from them represents the fourth constraint.

The fifth constraint relates to precipitation: a monitoring period suitable to recognize the role of the epikarst in the transport of pollutants from the karst surface to the saturated zone should include a hydrological stress able to trigger the flushing of the epikarst. Thus, a time-interval including a significant rainfall event following a period of low or null recharge should be selected.

Considering the above constraints, the study develops according to nine main steps. The steps from the first to the seventh were performed by GIS modelling.

The first step (Step 1) deals with the recognition of the endorheic basins. This target was achieved by GIS analysis of the Digital Elevation Model of Murgia (DEM with 8 m resolution, Regione Puglia, 2007). The drainage divide of the endorheic basins was obtained by forcing the recognition of drainage areas by defining real sink points, represented by the sinkholes, caves and graves present in the area. Particular attention was given to distinguish real sinks from artificial pits of the DEM. Generally, a DEM shows a large number of possible sink points, which are pixels entirely surrounded by other pixels of higher elevation. In most cases, the sink points are spurious, being caused by small differences in the original elevation data and by the method used for DEM generation. These spurious sinks should not be confused with endorheic areas, and represent a critical problem in hydrological applications as they interrupt continuous flow across the DEM surface. Therefore they are usually removed from DEM before deriving a river network by means of automatic procedures, which commonly consist in raising the elevation values of the cells inside the sink until an outflow point is encountered (Lehner *et al.*, 2006). Automatic procedures should not be used when dealing with karst systems because they do not distinguish spurious sinks from real endorheic areas. However, although suitable GIS procedures have been developed in the latest years, the sink evaluation process remains a long and critical task requiring specific expertise. The Arc Hydro Tools (Djokic, 2008) was adopted in this study for exploiting available maps of endorheic depressions: this way real sinks are forced to remain in the DEM, while false pits are removed by means of a classic filling operation.

The second step (Step 2) aims at recognizing the location of recharge areas. This step required the reconstruction of the aquifer thermal field. Groundwater temperature is very effective in tracing many hydrologic and hydrogeological processes in a variety of environments (Anderson, 2005). The interpretation of the 3D temperature distribution in terms of groundwater flow are based on the grounds that in topographically driven flow systems the forced advection disturbs the conductive thermal field leading to a temperature distribution, which is the result of a time-dependent exchange of heat between water and surrounding rocks (Domenico and Palciauskas, 1973). The extent of the hydrogeological disturbance depends on topography, climate, 3D water table configuration, basin geometry, magnitude and spatial distribution of permeability, hydraulic anisotropy and depth of active flow (Smith and Chapman, 1983; Woodbury and Smith, 1985; Forster and Smith, 1988; Dim *et al.*, 2002; Salem *et al.*, 2004). Thermal perturbations increase as the aquifer permeability or thickness increase: the most significant variations of the conductive thermal field can be observed, indeed, in fractured and/or karst aquifers, characterized by high anisotropy ratio of vertical to horizontal hydraulic conductivity (K_v/K_h). Thus, in such aquifers, the 3D isotherm trends that derives from the coupling of the conductive thermal field and the hydraulic field, can give information on the flow system, which in such aquifers cannot be reliably drawn on the base of hydraulic heads due to the high anisotropy of the medium (Jeannin, 1998, Kiraly, 2003; Post and von Asmuth, 2013). Temperature (T) data from logs carried out along the monitoring wells of the Regional Monitoring Net (Figure 2) set for the control of the quantitative and qualitative status of groundwater for the autumn 1995 were used for Kriging. T probes have a -5 to 50°C range, accuracy of ± 0.1°C and resolution of 0.01°C; temperatures were recorded at 0.5 m intervals of the saturated zone of the aquifer.

The third step (Step 3) involves the comparison of the location of endorheic basins with the location of the recharge areas: the comparison has the aim of selecting those endorheic basins that correspond to recharge areas.

The fourth step (Step 4) is about the choice of a suitable time interval including a precipitation series with a dry period and a subsequent hydrological stress. The selected time interval corresponds to August 1995, which is characterised by significant rainfall events: these rainfall events follow a dry period (null recharge) of four months. Monitoring Network of the Regional Hydrographic Services provided the daily precipitation data for the period are provided for 12 gauge stations (Figure 2).

<Figure 2>

The fifth, sixth and seventh steps concur to the modelling of nitrate concentrations in the waters of the autogenic recharge. The fifth step (Step 5) considers the land use of the selected endorheic basins. The land use maps derive from the SIGRIA (Information System for Water Management for Irrigation, INEA, 2001). SIGRIA database is available for GIS platforms and includes land use maps of the Regions of Southern Italy obtained by collecting data on irrigation infrastructures and on crop water requirements from Land Reclamation and Irrigation Consortia. The land use map for the study area is on 1:50.000 scale, and refers to the period 1996-1997.

The sixth step (Step 6) copes with the hydrologic modelling, i.e. the calculation of the amount of effective infiltration in the whole endorheic area during the chosen period. The whole Alta Murgia has a surface of 1446 km^2; the mean effective yearly infiltration (period 1950-2002) is 195 Mm^3 (135,1 mm/year), which represents the 21% of the mean yearly precipitation (943 Mm^3, 651,8 mm/year) (Portoghese *et al.* 2010). The hydrologic behaviour of endorheic areas in case of flood events has been studied by Iacobellis *et al*. (2015): in order to evaluate the real infiltration capacity, they used the classical Horton equation (Horton 1940) using the soil classification of the Soil Conservation Service Curve Number method (SCS 1972). The study area, according to the SCS classification, is characterised by soils with high potential infiltration after prolonged wetting (25.4 mm/h) and an initial potential infiltration rate as high as 250 mm/h. The methodology from Iacobellis *et al*. (2015) was not applicable to this study because only daily rainfall series are available. However, the comparison between the amount of the daily rainfall and the infiltration capacity of the soil allowed assuming that the rainfall events of August 1995 were not characterized by significant runoff volumes. Interception has been also considered negligible, since the vegetation cover is thin or absent. Thus, a basic water balance, where only evapotranspiration is subtracted from precipitation at the daily scale was used for the estimation of the effective infiltration occurred during August 1995. The values of potential evapotranspiration adopted in the hydrologic model derive from Canora *et al.* (2008). They collected data on Alta Murgia by means of a Class A evaporimeter for the estimation of the potential evapotranspiration (ET_{pan}) and compared ET_{pan} with the potential evapotranspiration rate (PET), calculated using Penman–Monteith method from meteorological data monitored daily between January 1st and December 31st 2004. The PET is available for shattered stone soil with wheat, for natural soil with typical pasture vegetation and bare karst.

The seventh step (Step 7) is about the calculation of the nitrate loads and the nitrate concentration (from evaluation of nitrate surplus) in the autogenic recharge water. These calculations considered every single endorheic basin, assuming that: (a) on a daily basis, all precipitation that exceeds evapotranspiration infiltrates, included the volumes related to runoff; (b) in presence of crops, nitrate surplus before the precipitation event is set equal to the total annual nitrate surplus; (c) all the nitrate surplus is leached by the total effective infiltration of August 1995. The nitrogen surplus was calculated on the base of the data reported in Table 1 (Regione Puglia, 2005), with nitrogen surplus being associated to each type of crop. Each value of nitrate surplus was multiplied by 0.8, as defined in the Safeguard Plan of Water Resources of Puglia Region (Regione Puglia, 2005), in order to consider the surplus of the only soluble component.

<Table I>

The location of the wells belonging to the Regional Monitoring Net (RMN) for the control of qualitative and quantitative status of groundwater in Alta Murgia (Figure 2) was examined during the eighth step with the aim of selecting those monitoring wells suitable to catch the autogenic recharge from the endorheic basins. In the period 1994-1997 the RMN for the entire Murgia area consisted of 54 wells, having a maximum depth of about 800 m b.g..

The comparison of the modelled nitrate concentrations in the autogenic recharge water (from Step 7) with the nitrate concentrations in groundwater is performed through the ninth step (Step 9). The latter data come from a monitoring survey carried out from the late 1994 to the early 1997 at selected wells of the RMN: this period includes the period selected for the study (Step 4). Sampling was performed with a four monthly frequency, though with some gaps, using stainless steel bailers equipped with a valve (non-pumping conditions). Sampling depth for each well was set a few meters below the top of the saturated zone. Groundwater samples were analysed in situ for pH, electrical conductivity (EC), redox potential (Eh), temperature (T), alkalinity. Major ions, nitrates, ammonium, phosphates, dissolved oxygen, total organic carbon (TOC), biochemical oxygen demand, chemical oxygen demand, silica, plumb, mercury, iron, and bacterial charge were analysed in laboratory within a few days from sampling. The first sampling survey occurred between March and May 1995, just before the rainfall events described in the fourth step (pre-event period), while a second sampling survey was carried out between September and October 1995, in the post-event period.

RESULTS

The results are reported according to the above methodological steps.

The application of the GIS procedure (Step 1) to Alta Murgia led to the recognition of 986 endorheic basins and sub-basins, characterized by a highly variable geometry and areal extensions ranging from a few km^2 to 99.5 km^2. Given their high number, in Figure 2 the endorheic basins and sub-basins are represented as a whole area.

The horizontal section of the thermal field at -5 m a.s.l. (Step 2) allows the recognition of the main recharge areas of Murgia aquifer. Figure 3 shows the horizontal Ordinary Kriging estimation of temperature distribution for the autumn-winter 1995: it allows the identification of two main recharge areas, one located to the NW and the other to the SW of the region. These recharge areas are outlined by the lowest temperatures (in the range 14 – 15.5°C) and the lowest horizontal thermal gradients. Such temperatures are slightly higher than the average atmospheric temperature during the autumn-winter recharge period (10.1 °C). Information on the recharge areas of Murgia aquifer gained by the interpretation of thermal field matches the results obtained by the application of chemical and isotope natural tracers (Tulipano *et al.*, 1990). In the two recharge areas, where infiltration water moves towards the saturated zone both through matrix and main vertical fractures/joints and swallow-holes, the temperature logs, as expected (Chengjie, 1988; Ravnik and Rajver, 1998), show vertical temperature gradients mainly close to zero or even negative (Tulipano and Fidelibus, 1989; Fidelibus and Tulipano, 2005).

<Figure 3>

Figure 3 also shows that the location of most endorheic basins corresponds in great part to the areas contoured by the 15.5°C isotherm (Step 3). Given their high number and limited single extension, Steps 4 to 7 are applied to the whole endorheic area shown in Fig 3.

The precipitation data regarding the January 1995 – December 1996 period (Figure 4a) from the selected 12 pluviometric stations (Figure 2) show that the rainfall events occurred between the 16th and 20th of August 1995 were quite significant for their spatial extent and interested the entire endorheic area. All the stations registered the events, with peaks in the areas surrounding Mercadante (65.2 mm/day) and Grumo Appula (46.6 mm/day) stations on August 18 (Figure 4b).

The max daily rainfall of 48 mm (at the Minervino Murge station) and 42.2 mm (at the Corato station) characterised the event of August 16. Sub-daily rainfall data published by the Regional Hydrographic Services are only available from annual maximum rainfall series of different durations: data recorded at Mercadante and Grumo Appula stations show that the rainfall event occurred on August 18 was characterized by duration of about 12 hours (64.6 mm) and 6 hours (37 mm) respectively. The return time of the event in terms of rainfall intensity is about 5 years, which is not very high with respect to the singular time series observed at rain gauges in the area. However, at four stations (Mercadante, Grumo Appula, Altamura and Andria) this was recorded as the annual maximum rainfall event in 1995.

<Figure 4a and b>

The Step 7 deals with the estimation of the nitrate concentrations (nitrate surplus) in the autogenic recharge waters for each endorheic basin; the estimation is achieved by using the land use map (Step 5, >) and the calculated effective infiltration (Step 6) for the selected time window (August 1995). The land use map of the study area (Figure 5) shows 58% of croplands, 40% of forests and natural vegetation and 2% of urban areas. Croplands are mainly occupied by permanent crops: not irrigated arable land, orchards, olive groves, and vineyards (54%) are characterized by high inputs of nitrogen fertilizers. The soluble nitrogen (surplus) was transformed in nitrate (NO_3^-), thus obtaining the nitrate load per m^2 in relation to each type of crop (Figure 6a). For every single endorheic basin, the nitrate concentrations in the autogenic recharge derive from the dilution of the total nitrate load in the related volume of effective recharge within the selected time window (Figure 6b). The 46% of the endorheic area shows concentrations less than 50 mg/L, while the 22% shows concentrations between 50 and 100 mg/L; concentrations between 100 and 500 mg/L characterise the 29% of the remaining area, with only 2.7% with concentrations higher than 500 mg/L. The average concentration of nitrates in the whole volume of the autogenic recharge of the period (modelling Step 7) is 54 mg/L.

<Fig 5>

<Fig 6a and 6b>

The wells considered for the study (Step 8) were selected among those of the Monitoring Net (Figure 2) under the criterion of having the highest chance to directly catch the autogenic recharge: the selected wells are close to (or in direct correspondence of) the endorheic basins.

For the aims of Step (9), Figs. 7a, 7b, 7c, 7d, and 7f respectively show the time trend of nitrates, calcium, TOC, magnesium concentrations, and Mg/Ca ratio with reference to groundwater samples taken at the selected wells of the RMN during the monitoring period. Figure 7e shows the variation of the hydraulic heads measured at the same wells during the same period. For the needed reference, Fig. 7g shows the monthly precipitation in the 12 gauge stations regarding the same monitoring period.

<Figs. 7a, 7b, 7c, 7d, 7e, 7f and 7g>

Nitrate concentrations (Figure 7a) are around 5 mg/L before the rainfall event (May-June 1995): such concentrations are close to the natural background concentrations (about 4-5 mg/L). The nitrate concentrations increase up to maximum values of 60 mg/L after the hydrological stress of August 1995 (Figure 4b), then they decrease. The increase in concentration occurs after a mean delay of two months. Really, without samplings in between the two dates it is incorrect to assert that the post-event peaks of nitrates occur with a mean delay of two months from the rainfall events. In fact, the post-event sampling may have intercepted either an ascending pre-peak phase or a descending post-peak phase. However, the high nitrate concentrations in the post-event period remain a fact: these high concentrations should characterize water stored in the epikarst in the pre-event period (non-recharge period), with accumulation of nitrates. The time elapsed between the rainfall events and the post-event peaks of nitrates in ground waters may only indicate that the transfer time of water volumes stored in the epikarst to saturated zone through the network of fractures and/or conduits that by-pass the less permeable unsaturated zone is within the two months. The displacement of the epikarst water occurs under piston effect. Precipitation of winter 1995 (Figure 4a), characterized by a total volume considerably higher than the volume of August 1995 precipitation, does not cause any increase of nitrate concentrations in ground waters.

The nitrate concentrations measured in ground waters sampled in the 11 wells of the RMN during the post-event time are in the range 10 – 60 mg/L. These concentrations are comparable to the nitrate concentrations of the autogenic recharge waters resulting from modelling (Steps 6 and 7, Figs. 6a and 6b) for the endorheic basins more close to the wells, and to the average nitrate concentration of 54 mg/L characterising the whole volume of the autogenic recharge.

After October 1995, the monitoring does not follow the previous frequency, thus preventing the evaluation of the quality of groundwater after another significant rainfall event, which occurred in September 1996 following a low recharge period similar to that of August 1995. However, monitoring data from other wells of the RMN of Puglia Region (recharge areas of Salento Peninsula, outside the study area) indicate that the nitrate concentration in September 1996 follows the same trend observed before and after the rainfall events of August 1995 in the Murgia recharge area.

The time trends of the Total Organic Carbon (TOC) (Figure 7c), mirror those of nitrates: the post-event concentrations are about one order of magnitude lower than those in the pre-event period. In the case of karst systems not polluted from specific human sources and not directly fed by river water, TOC derives from the soil biological activity: organic content of soil water can attain the 300 mg/L, while TOC does not exceed the 100 mg/L in river water. These features make TOC a suitable tracer of rapid infiltration. An increase of TOC at a karst spring during a flood indicates the arrival of water of low residence time, while TOC concentrations lower than previous during spring recession indicate higher residence time (Emblanch *et al*., 1998; Batiot, 2002; Bakalowicz, 2003; Batiot *et al*., 2003).

The increase of nitrates and the contemporary decrease of TOC observed after the rainfall events of August 1995 corroborate the hypothesis that ground waters are recharged from a reservoir (the epikarst) where the water spent adequate time to allow organic matter degradation and build-up of non-reactive species.

Other natural tracers help in substantiating the hypotheses about the mass transport mechanism. Figs. 7c and 7d respectively show the time trends of calcium and magnesium concentrations in ground waters. In the post-event period, the magnesium concentrations increase and calcium concentrations decrease: thus, the Mg/Ca (molar) ratio increases (Figure 7f). The Mg/Ca ratio varies across carbonate aquifers reflecting the stages of reaction with dolomite and calcite: ground waters readily react with calcite, then they incongruently react with dolomite (having slower dissolution kinetics than calcite) giving increased Mg/Ca with increasing age of water (Edmunds and Smedley, 2000; Plummer *et al.*, 1978). Thus, the increase of Mg/Ca ratio indicates that sampled ground waters do not derive from recent infiltration. Figs. 7b, 7d and 7f show that the recharge of the autumn-winter 1995-1996 causes the opposite, i.e. the increase of calcium, the decrease of magnesium, and the decrease of Mg/Ca ratio.

Hydraulic heads were measured at the considered wells just before each sampling. The hydraulic heads do not increase after August 1995, being sometime even lower than the hydraulic heads during the pre-event period: hydraulic heads increase only after the winter recharge (November 1995 - March 1996). To enhance these variations, Figure 7e shows the difference between each measure of hydraulic head and the previous one; first measures were carried out between December 1994 and April 1995. The variations of hydraulic heads shown in Figure 7e indicate that the polluted water volumes reaching groundwater after the rainfall event of August 1995 are negligible compared to those of the winter recharge.

DISCUSSION

The presence of 986 endorheic basins, each including one or more sinkholes, And the correspondence between the location of the endorheic areas and the lowest temperatures of the aquifer thermal field define the Alta Murgia territory as an autogenic recharge area. The study on the mechanisms of mass transport from the karst surface to the saturated zone relied on a set of favourable conditions: a time interval, including a low-recharge period and a subsequent hydrological stress, and the presence in the recharge areas of a few wells of the RMN where sampling of ground waters occurred in the same time interval.

The average nitrate concentration of the waters of the autogenic recharge, obtained by modelling for this time interval (54 mg/L, Step 5), is within the range of the nitrate concentrations measured in ground waters sampled after the hydrological stress (10-60 mg/L, Steps 6 and 7). This fact confirms that sampled ground waters derive from the autogenic recharge in the endorheic area.

Results of Steps from 1 to 9 allow developing a conceptual model about the mechanisms of recharge and mass transport acting within the Alta Murgia karst system. Figure 8 shows a sketch of such conceptual model based on a simplified SE-NW geological section of the study area (trace AA' in Figure 2): it includes schematic information on the main geological, geomorphological and hydrogeological features of the area.

<Figure 8>

Figure 8a (pre-event period) outlines the situation during summer season: during this period of low recharge, non-reactive pollutants, as nitrates, accumulate in the epikarst, while organic matter oxidises and water-rock interaction determine progressive evolution of waters.

A few significant rainfall events following the period of low recharge cause the saturation of the epikarst (event and post-event period, Figure 8b): thus, water stored in the epikarst and conduits during the low recharge period flow towards the saturated zone, conveying the pollutant (reactive and non-reactive) load. Nitrate concentrations and Mg/Ca ratios related to the ground water sampled in the post-event period are both higher than those characterising the pre-event period, while TOC decreases. In the post-event period, the hydraulic heads do not significantly increase with respect to the pre-event hydraulic heads.

All the findings indicate that the effective infiltration after the significant rainfall events consists of water volumes, which produce insignificant hydraulic head variations: however, ground waters have peculiar features that indicate that they have resided for enough time in the reservoirs overlying the unsaturated zone to allow non-reactive pollutant accumulation, water-rock interaction and organic matter degradation.

The autumn precipitation, which follows the summer hydrological stress, progressively leaches the epikarst (Figure 8c), which continues behaving as a perched aquifer with a horizontal flow towards conduits, sinkholes and master joints. Due to continuous leaching, the water flowing within the epikarst becomes progressively younger than the water originally stored. The winter precipitation finds the epikarst completely leached: the recharge waters move forward through the entire unsaturated zone of low permeability. In this period, groundwater concentrations of nitrates and magnesium decrease, while calcium concentrations increase. The hydraulic heads increase only after the autumn-winter recharge, with an apparent time lag from two to four months with respect to the post-event nitrate peaks.

CONCLUSIONS

Considering a reference time window including a period of low recharge (coinciding with the fertilization period) followed by significant rainfalls, the study proves the agreement between the range of variation of nitrate concentrations measured in ground waters and the mean concentration of nitrates in the autogenic recharge waters resulting from modelling.

This agreement substantiates the hypothesis about the role of both the endorheic basins and the epikarst storage in the recharge processes and mass transport in the karst aquifer of Alta Murgia.

The role of the epikarst in the direct transfer of nitrates (used in the study context as tracers of mass transport) from the karst surface to the saturated zone in the Alta Murgia karst system is evident after a hydrological stress, which follows a low recharge period. During this low recharge period, pollutants accumulate and/or degrade in the epikarst, while infiltration waters evolve due to water-rock interaction. The epikarst behaves as a mediator of the recharge process: this fact replies to the first research question. Under the following hydrological stress, the epikarst returns at once to groundwater what previously stored. The hazard of pollution for groundwater is temporary, but significant: it is mainly connected to the semi-arid features of local climate and the peculiar geomorphological features defined by the endorheic nature of the recharge area. Such a type of hazard implies the occurrence of subterranean “flash-floods” similar to the superficial ones. The “superficial flash flood” displaces and conveys to groundwater the water volumes and the related pollutant loads stored in the epikarst zone during low recharge periods. These water volumes, having peculiar chemical features, are, however, irrelevant compared to the recharge volumes of the autumn-winter recharge period. According to such conceptual model of mass transport, a series of minor rainfall events, even close, whose volume does not saturate the epikarst, should not cause significant variations of groundwater quality. During the autumn-winter recharge, the epikarst is already totally leached and the large volumes of recharge water coming from the whole unsaturated zone dilute groundwater concentrations.

The above information reveals useful in interpreting the dynamics of pollution in the study area. Thus, the recognition of the presence of the epikarst becomes an important element for intrinsic vulnerability mapping and its validation. All above respond to the second research question. Moreover, the described facts encourage further research, with the aim of extend the study to the other parts of the region (out of the main recharge areas) where the covers and the prevailing horizontal flow of groundwater add elements of complexity to the already complex system.

Concerning the third research question on the type of methodological approach to use for the study of mass transport mechanisms in platform karst systems having a regional dimension and without freshwater springs, the results show that the combination of classical and novel methods figures out with efficacy. The behaviour of the studied system is very different from that of karst systems of local or medium scale, which quickly respond to recharge input: its large hydraulic inertia entails a lag of at least two months between the start of the autumn-winter recharge and the increase of piezometric heads. Groundwater monitoring should be always planned according to the system dynamics and, in this case, a monthly frequency of monitoring would have been more effective than the four-monthly monitoring frequency adopted in the period 1995-1997. Unfortunately, monitoring frequency further decreased after 1997, due to the very high costs, and no other data are currently available.

Notwithstanding the uncertainty connected to the monitoring frequency, the results of the study are relevant because they were obtained despite all the difficulties intrinsically connected to the study of a complex karst coastal aquifer of large size, lacking of freshwater springs and with a regional flow system.

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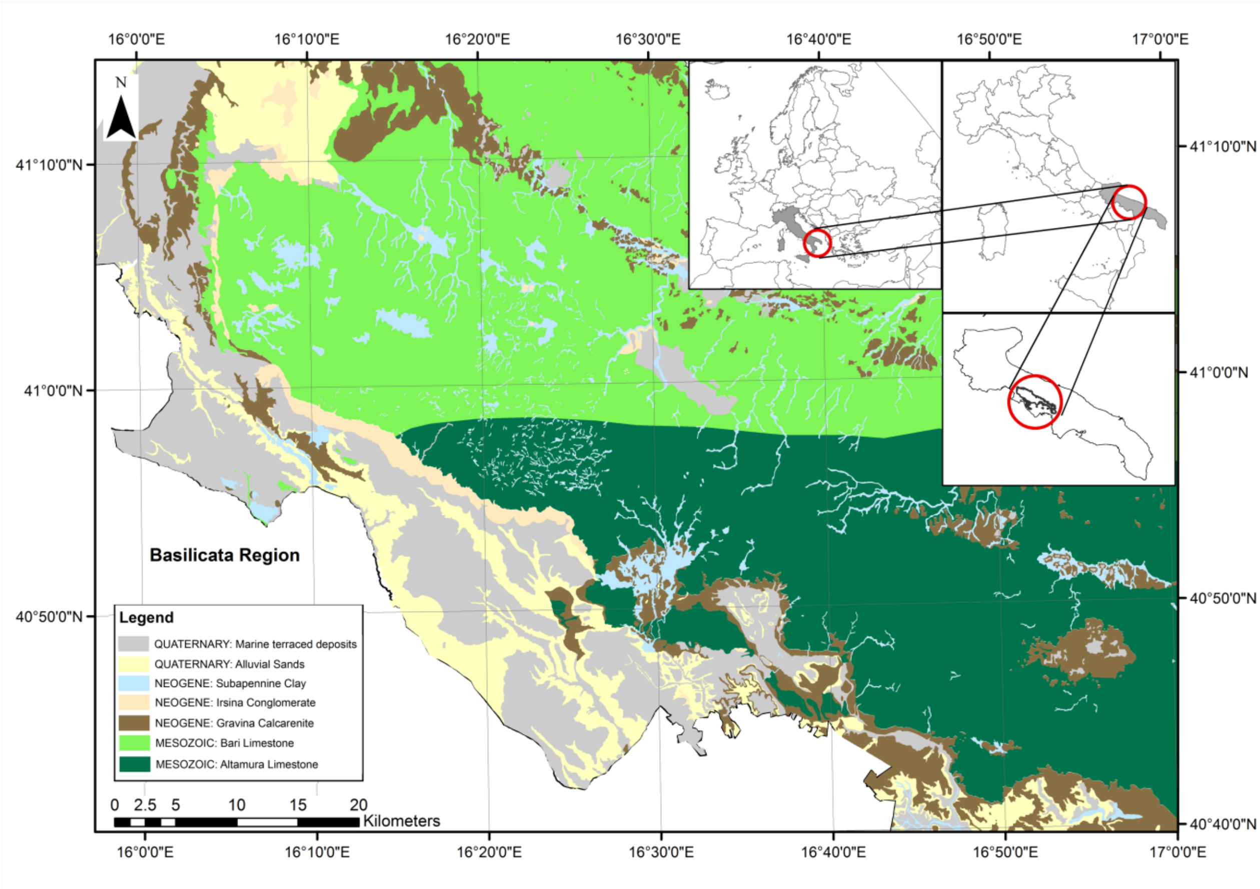

Figure 1 Location and schematic geological features of the study area

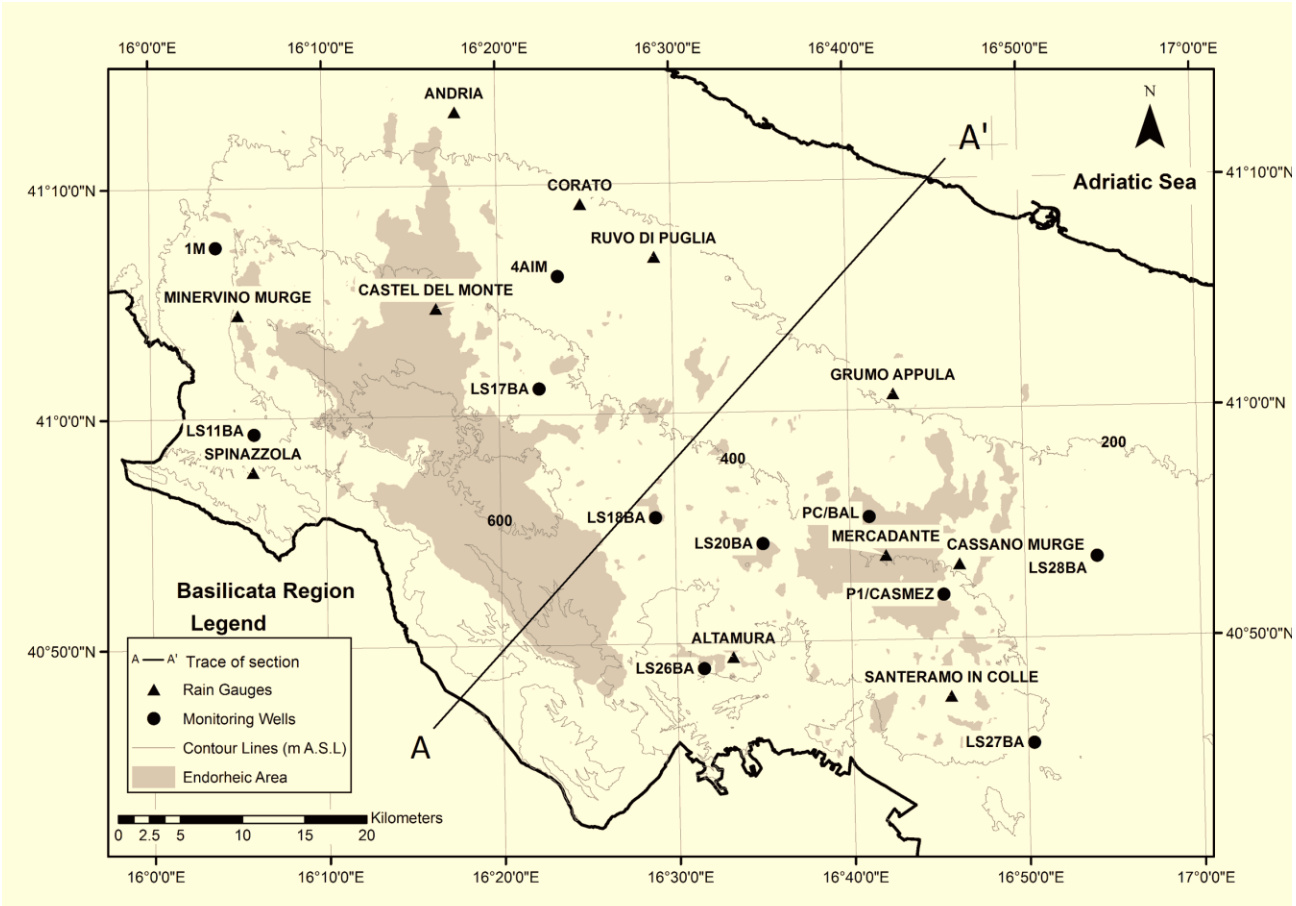

Figure 2 Outline of the endorheic areas in Alta Murgia; location of rain gauge stations and groundwater monitoring wells

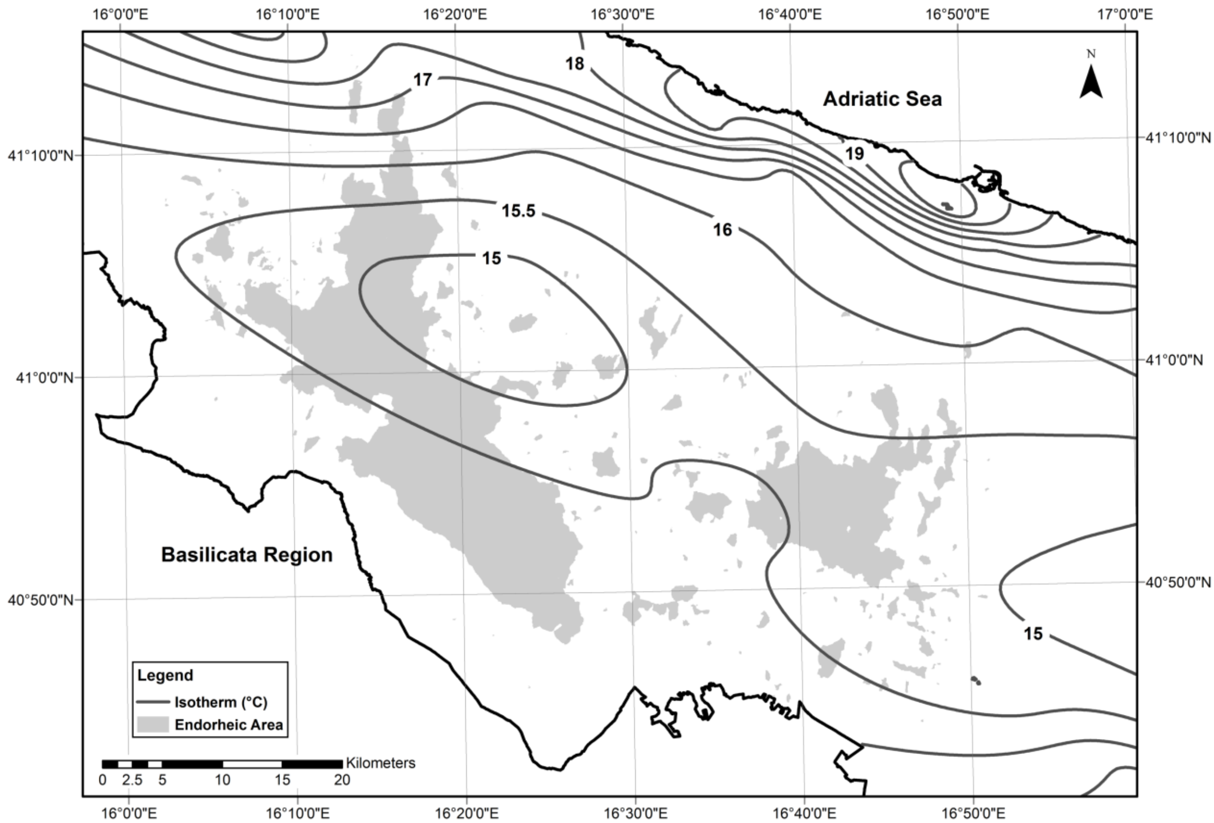

Figure 3 Horizontal Ordinary Kriging estimation of the temperature distribution at -5 m a.s.l. (from Fidelibus et al 2010, modified); the location of the main recharge areas (included by the isotherm 15.5 °C) is compared to the location of endorheic areas

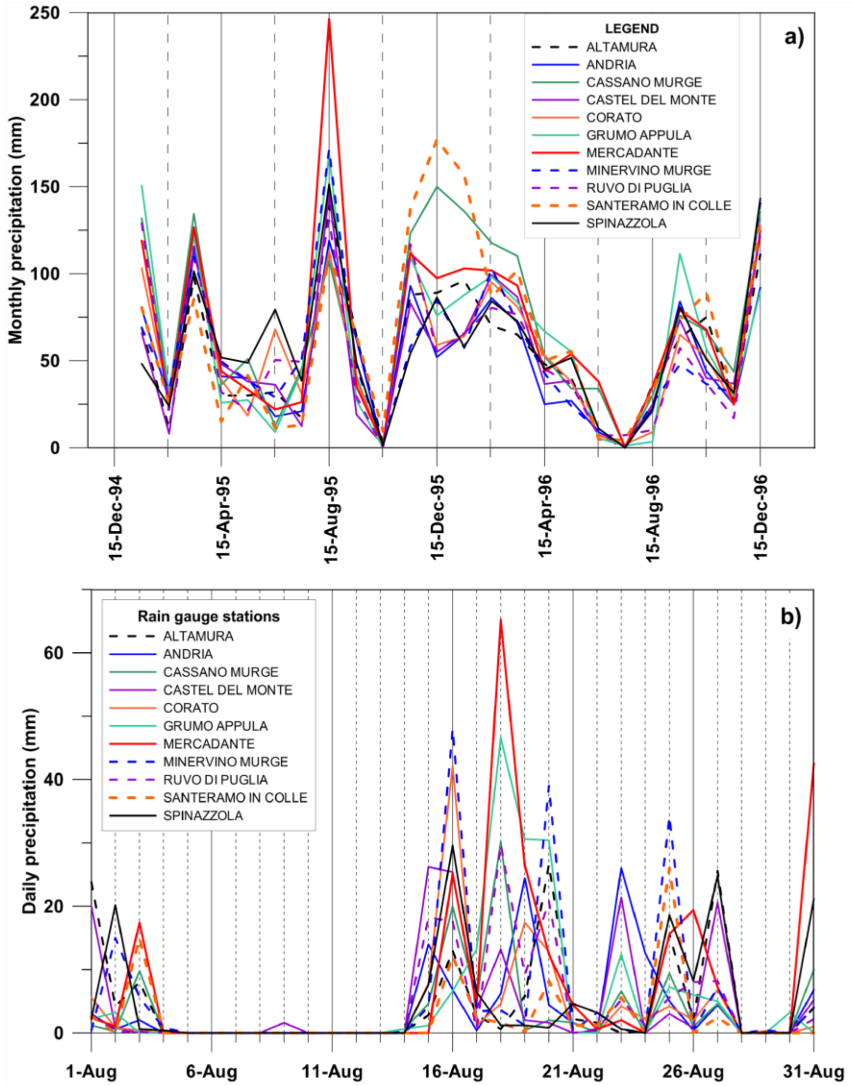

Figure 4 a) Monthly precipitation in the period January 1995-December 1996 recorded at the gauge stations located in the study area (location in Figure 2); b) daily precipitation during August 1995 at the same stations

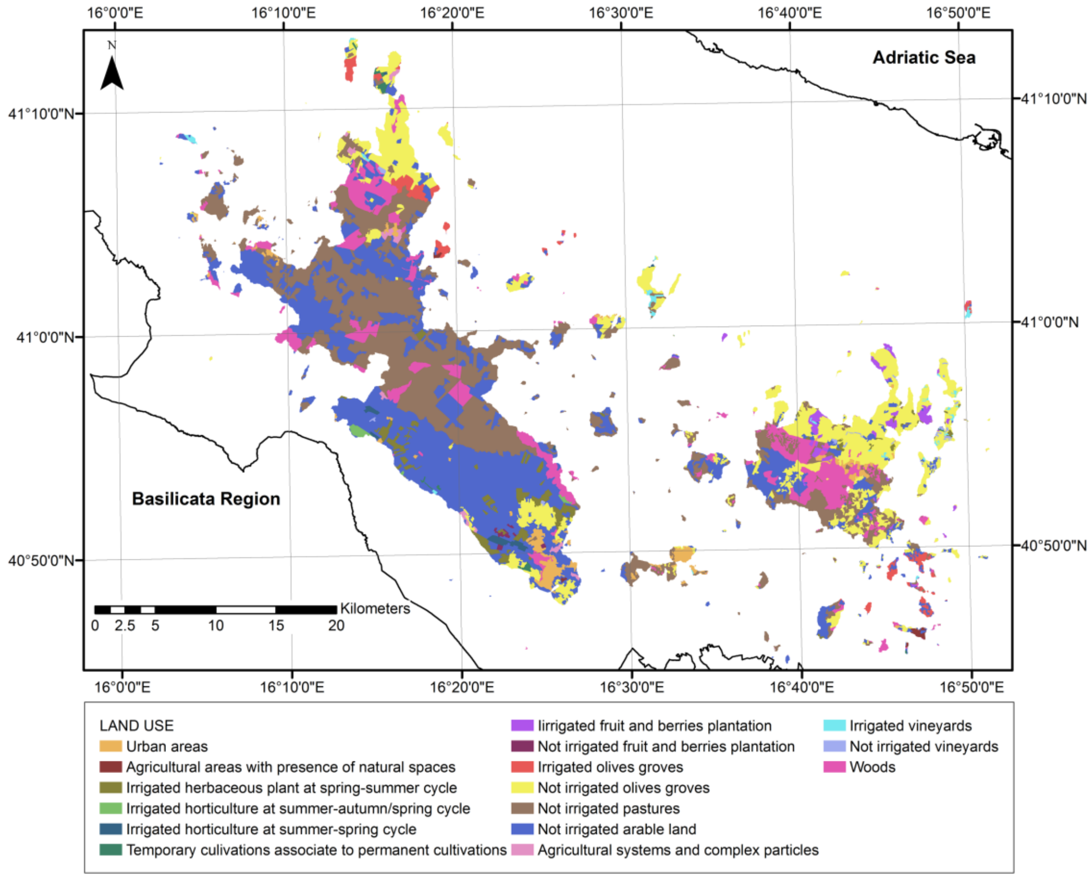

Figure 5 Land use in the endorheic basins (elaboration of data from INEA, 2001)

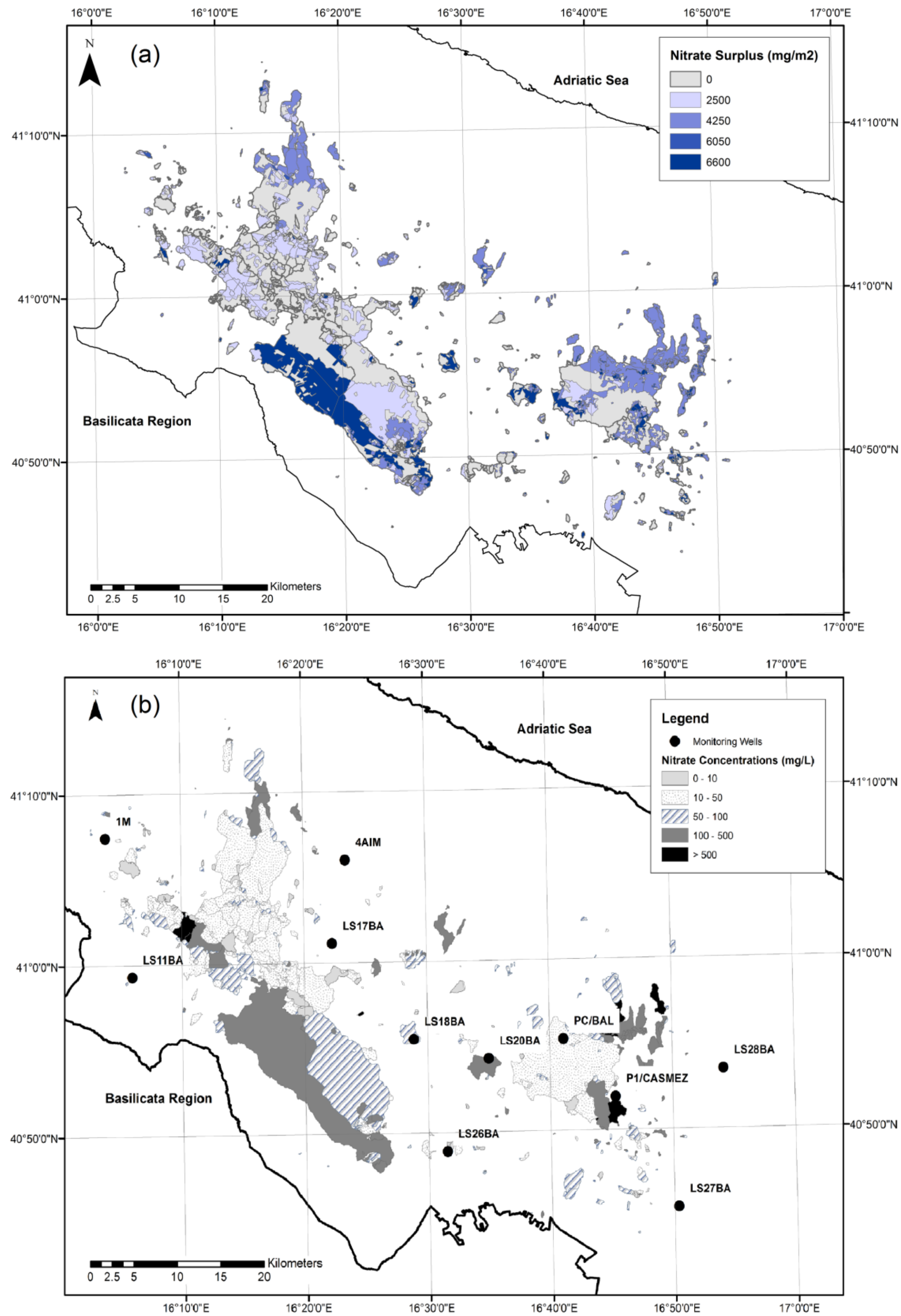

Figure 6 Nitrate surplus (mg/m^2) (a) and nitrate concentrations (mg/L, modelled values) (b) in the autogenic recharge water

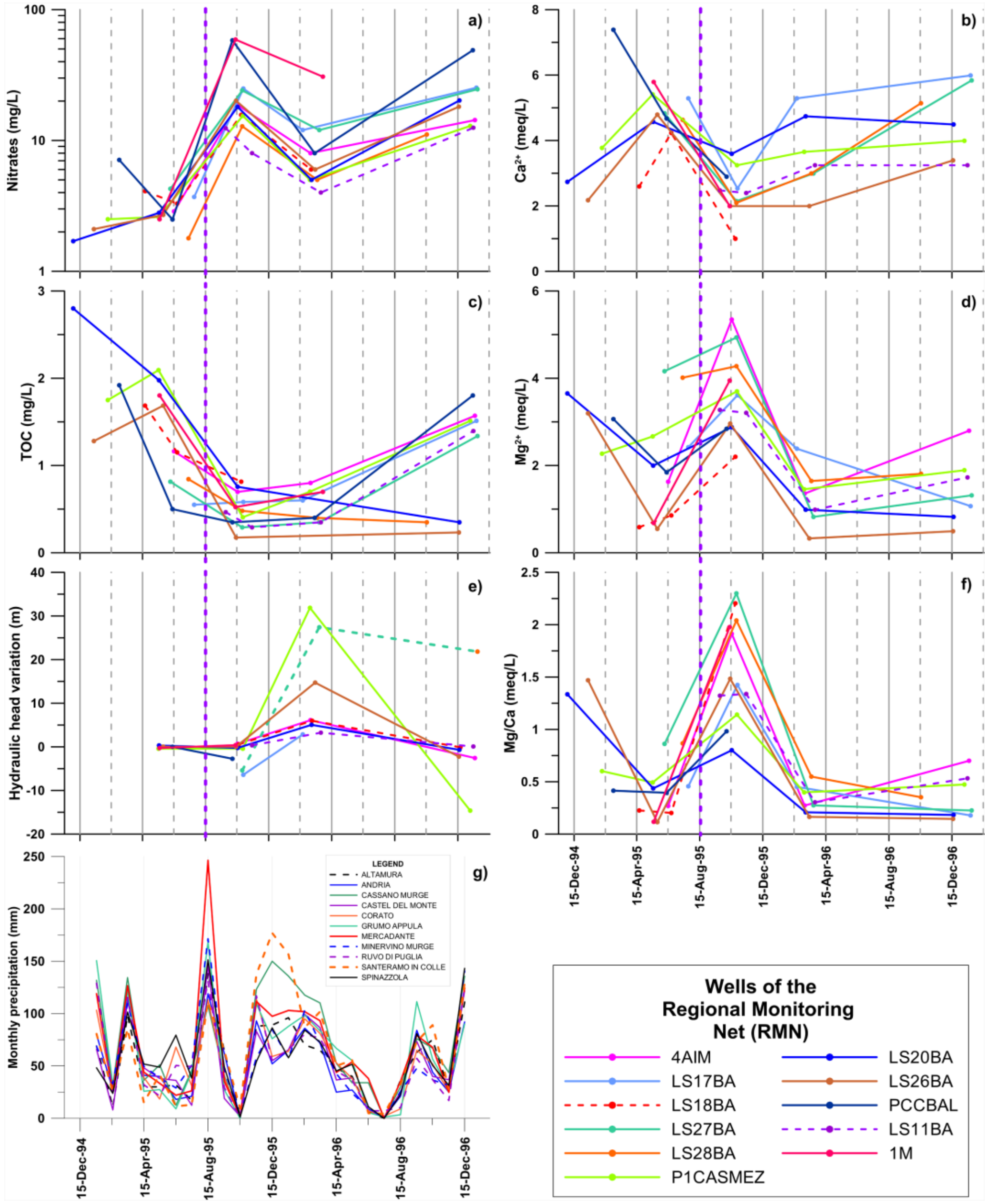

Figure 7 Time trends of: a) nitrate concentration (mg/L), b) calcium concentration (meq/L), c) TOC concentration (mg/L), d) magnesium concentration, and f) Mg/Ca ratio in the waters sampled at the wells in the Regional Monitoring Net from the end of 1994 to the beginning of 1997; e) variation of hydraulic heads in the same period; g) monthly precipitation in the period January 1995-December 1996 recorded at the gauge stations located in the study area. The dotted line in a), b), c), d), e) and f) indicates the mean position of the hydrological stress.

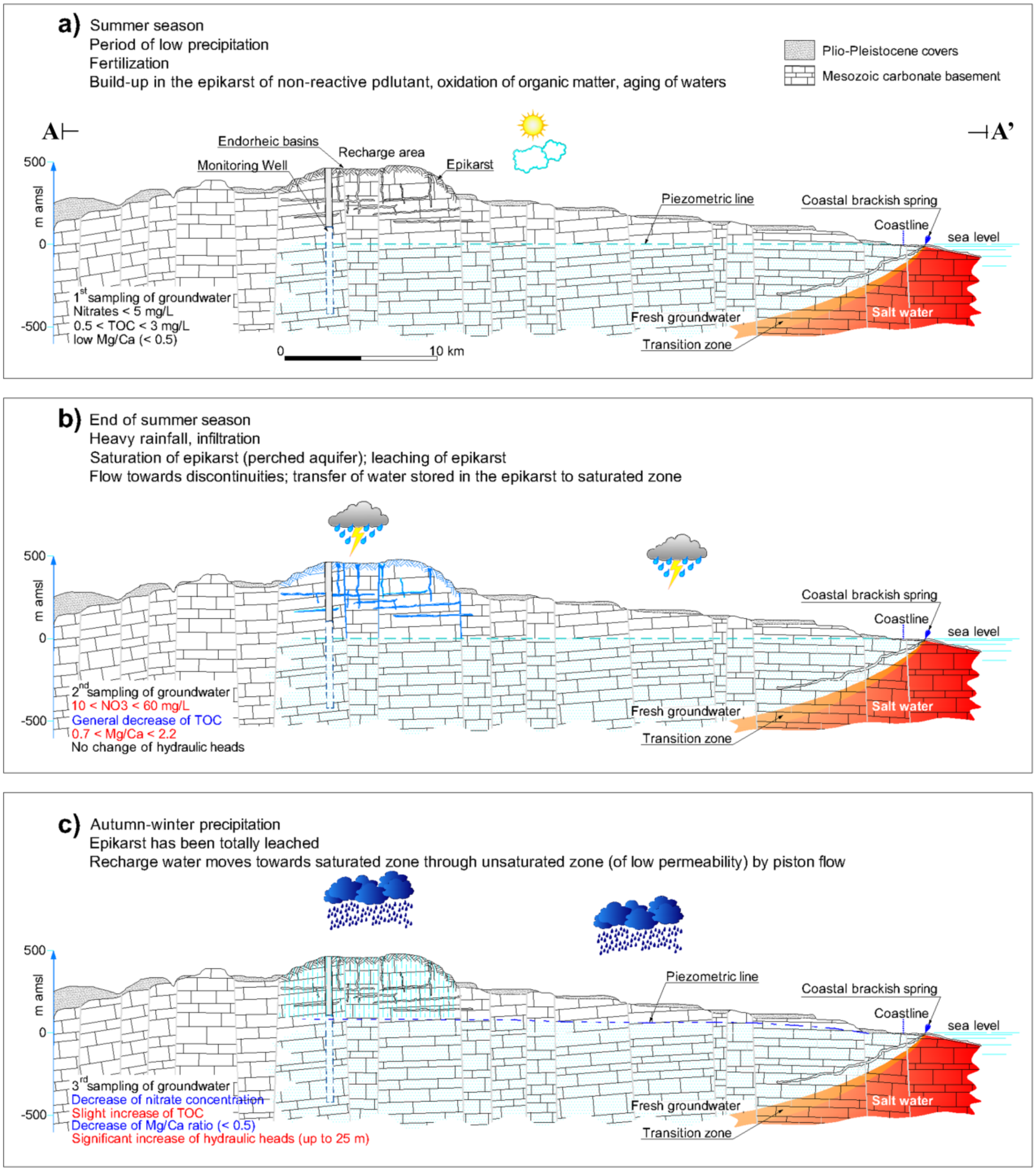

Figure 8 Sketch of the conceptual model: a) pre-event period (summer season); b) event and post-event period (end of summer season); c) autumn-winter period. The geological section of the study area (trace AA' in Figure 2) is modified from Doglioni et al. (2006).

Table 1 Land use and related Nitrogen surplus (Regione Puglia, 2005)

Land Use	Nitrogen Surplus (kg/ha)	Nitrogen Surplus (mg/m^2)	Soluble N (mg/m^2)	Soluble NO_3 (mg/m^2)
Irrigated horticulture at spring-summer cycle	0	0	0	0
Irrigated horticulture at summer-autumn or summer-spring cycle	0	0	0	0
Not irrigated arable land	25	2500	2000	8857
Agricultural systems and complex particles	25	2500	2000	8857
Not irrigated Fruit and berries plantation	42.5	4250	3400	15057
Irrigated Fruit and berries plantation	42.5	4250	3400	15 057
Irrigated Vineyards	60.5	6050	4840	21 434
Not irrigated Vineyards	60.5	6050	4840	21 434
Not irrigated Olive grove	66	6600	5280	23 382